Soap-Based Detergent Formulations: VIII. N-Alkylsulfosuccinamates as Lime Soap Dispersants[1]

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ABSTRACT

A series of sodium methyl N-alkylsulfosuccinamates was prepared by the reaction of methyl N-alkylmaleamates with sodium bisulfite in aqueous ethanol. The surface-active properties and detergency of these derivatives were compared with those of a series of disodium N-alkylsulfosuccinamates prepared by the reaction of sodium sulfite with N-alkyl-maleamic acid in water. The ester derivatives generally showed good lime soap dispersing requirement and washing ability in combination with soap, whereas the disodium salts were somewhat deficient in these properties and exhibited good washing ability only at 0.2% concentration with the surfactant as the sole component.
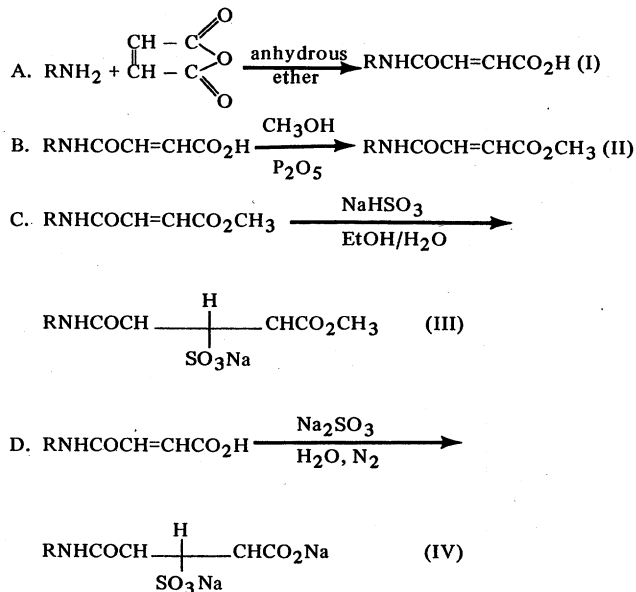
INTRODUCTION

Soap is an excellent washing agent in soft water; however, the formation of insoluble calcium curd in hard water leads to redeposition of soil on the fabric and, therefore, to a substantially poorer performance than is found with today's phosphate built synthetic detergents. This problem can be minimized by using soap in combination with lime soap dispersing agents (LSDA) which act principally to prevent curd formation in hard water by maintaining the soap in colloidal suspension.

LSDA were described by Stirton, et al., (1) as substances consisting of a long hydrocarbon chain (16-18-carbon atoms) terminated by a large hydrophilic group. The water-soluble moiety should contain two or more hydrophilic functions. Recent studies from this laboratory by Bistline, et al., (2) and Noble, et al., (3) showed that several LSDA-soap-builder formulations exhibited excellent detergencies for high soap concentrations. Many of these combinations containing a sodium silicate builder performed as well in hard water as a standard heavy duty household detergent used as a control.

Sulfosuccinamate derivatives have received little or no attention as LSDA. The literature contains several patents (1941-1962) dealing with the synthesis and use of a variety of sulfosuccinamates, consisting principally of disodium salts, where the hydrogen atoms on nitrogen are substituted with alkyl groups or an alkyl group and a succinyl ester radical. In a basic patent, Jaeger (4) synthesized sodium octyl N,N-dipentylsulfosuccinamate, a compound closely related to our present work.

In this study, primary alkyl amines were reacted with maleic anhydride to yield the N-alkylmaleamic acids (I) in essentially quantitative yields. The N-alkylmaleamic acids then were esterified with methanol in 90% yields to the methyl esters (II) or could be treated directly with sodium sulfite to form the disodium N-alkylsulfosuccinamates (IV) in 80% yields. Finally, the methyl esters (II) were treated with sodium bisulfite to form sodium methyl N-alkylsulfosuccinamates (III) in 80% yields. The overall approach is summarized in equations A-D.

A. $RNH_2 + \begin{matrix} CH-C \\ \| \\ CH-C \end{matrix} \begin{matrix} O \\ O \\ O \end{matrix} \xrightarrow[\text{ether}]{\text{anhydrous}} RNHCOCH=CHCO_2H$ (I)

B. $RNHCOCH=CHCO_2H \xrightarrow[P_2O_5]{CH_3OH} RNHCOCH=CHCO_2CH_3$ (II)

C. $RNHCOCH=CHCO_2CH_3 \xrightarrow[EtOH/H_2O]{NaHSO_3}$

$$RNHCOCH \overset{H}{\underset{SO_3Na}{\vert}} CHCO_2CH_3 \quad (III)$$

D. $RNHCOCH=CHCO_2H \xrightarrow[H_2O, N_2]{Na_2SO_3}$

$$RNHCOCH \overset{H}{\underset{SO_3Na}{\vert}} CHCO_2Na \quad (IV)$$

We have attempted to correlate the structure of derivatives III and IV with their surface-active properties. The principal objective was to evaluate these compounds in LSDA-soap and LSDA-soap-builder formulations to achieve detergencies comparable to those of commercial phosphate built detergents.

EXPERIMENTAL PROCEDURES

Materials

The fatty amines were purified by vacuum distillation through a 2 ft column of protruded packing under a nitrogen atmosphere. Gas chromatography showed the center cuts to be better than 98% pure. Tallowamine (neutral equivalent [NE] 272) was Armeen-T from Armak Chemicals Division, Akzona, and was used as such without purification.

Methods

N-alkylmaleamic acid (I): This preparation was based upon a procedure by Mehta, et al. (5). To a liter flask equipped with a stirrer, reflux condenser, dropping funnel, and a drying tube was added 14.7 g (.15 mole) maleic anhydride and 300 ml anhydrous ether. After complete dissolution of the anhydride, a solution of 32.0 g (.15 mole) tetradecylamine in 250 ml anhydrous ether was added at such a rate (5-10 min) as to maintain reflux. After the amine addition had been completed, the mixture was refluxed for 3 hr and allowed to stand overnight at room temperature. The reaction mixture was filtered by suction, and the solid was air dried to give essentially a quantitative yield of N-tetradecylmaleamic acid, melting point (mp) 99-100 C, found neutral equivalent 310.5, theory 312. The other homologous maleamic acids where R is dodecyl, hexadecyl, and octadecyl had mp's of 94-95 C, 101-103 C, and 103-105 C, respectively. The compounds were obtained in better than

TABLE I

Elemental Analysis of Sodium Methyl N-alkylsulfosuccinamates

N-alkyl-substituent	Percent carbon		Percent hydrogen		Percent nitrogen		Percent sulfur		Percent sodium	
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
$C_{12}H_{25}$	50.85	50.69	8.04	7.93	3.49	3.34	7.99	8.26	5.73	5.74
$C_{14}H_{29}$	53.13	53.24	8.45	8.32	3.26	3.08	7.46	7.30	5.35	5.18
$C_{16}H_{33}$	55.11	55.19	8.81	8.94	3.06	3.09	7.01	6.83	5.02	4.93
$C_{18}H_{37}$	56.88	56.05	9.13	9.08	2.88	2.74	6.60	6.68	4.73	4.59
Tallow[a]	56.22	56.62	9.01	9.23	2.94	2.78	6.75	6.72	4.84	4.91

[a]Theoretical tallow values are based upon the approximate composition of 37% C_{16} component and 63% C_{18} component.

TABLE II

Elemental Analysis of Disodium N-alkylsulfosuccinamates

N-alkyl-substituent	Percent carbon		Percent hydrogen		Percent nitrogen		Percent sulfur		Percent sodium	
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
$C_{12}H_{25}$	46.93	47.49	7.14	7.42	3.42	3.26	7.83	8.08	11.23	11.32
$C_{14}H_{29}$	49.41	49.50	7.60	7.62	3.20	3.12	7.32	7.57	10.51	10.53
$C_{16}H_{33}$	51.60	51.21	8.01	8.13	3.01	2.92	6.89	7.14	9.88	9.92
$C_{18}H_{37}$	53.53	53.19	8.37	8.62	2.84	2.75	6.50	7.10	9.32	9.30
Tallow[a]	52.81	52.49	8.23	8.22	2.90	2.81	6.65	7.06	9.53	9.67

[a]Theoretical tallow values are based upon the approximate composition of 37% C_{16} component and 63% C_{18} component.

95% yields and had neutral equivalents which agreed within 2 units with the theoretical values. They were prepared in the same manner; however, the quantity of solvent was adjusted to give stirrable mixtures.

Methyl N-alkylmaleamate (II): This method is a variation of the procedures used by Schwartz (6) to prepare analogous derivatives. To a liter flask flushed with dry nitrogen and equipped with a stirrer, condenser, and drying tube was added 400 ml absolute methanol and 20.0 g (.064 mole) N-tetradecylmaleamic acid. The mixture was cooled in an ice bath and 30 g (.21 mole) phosphorus pentoxide was added portionwise. The mixture was warmed to 40 C for 1 hr and then stirred overnight at 25 C. After evaporation of one-half of the methanol at reduced pressure, the crude product was precipitated by cooling to -30 C, and the mixture was filtered. The crystalline solid was dissolved in 200 ml chloroform, and the solution was washed with water to neutrality. The chloroform solution was filtered by gravity and evaporated to dryness on a steam bath. The residue was crystallized from 100 ml methanol to yield 19 g (91% yield) methyl N-tetradecylmaleamate, mp 78-79 C. The remaining methyl esters, where R is dodecyl, hexadecyl and octadecyl, had mp's of 69-70.5 C, 79-80 C, and 83-84 C, respectively. These esters were similarly prepared in yields of 90%.

Sodium methyl N-alkylsulfosuccinamate (III): The following procedure was applied in the preparation of all derivatives shown in Table I with minor changes in the quantity of solvents used. To a 100 ml flask equipped with a condenser was added 10 ml water and 3.85 g (.037 mole) sodium bisulfite. After the salt had dissolved, 12.0 g (.037 mole) methyl N-tetradecylmaleamate was added along with 20 ml 95% ethanol. The mixture was refluxed 1 hr on the steam bath, filtered hot by suction, and treated with 25 ml 95% ethanol. The solution was cooled in an ice bath and the precipitated solid then was filtered and vacuum dried at 50 C and < .1 mm pressure to yield 14.0 g solid. The crude product was dissolved in 150 ml hot 95% ethanol and filtered. The filtrate was evaporated under vacuum to constant wt yielding 12 g (75% yield) sodium methyl N-tetradecylsulfosuccinamate. The remaining derivatives, whose elemental analyses are shown in Table I, were obtained in 70-95% yields.

Disodium N-alkylsulfosuccinamate (IV): To a 250 ml flask equipped with a stirring bar, nitrogen bubbler, and reflux condenser was added 60 ml water. The water was

TABLE III

Surface-Active Properties of Disodium N-alkylsulfosuccinamates

N-alkyl-substituent	LSDR[a]	Krafft point C	Calcium ion[b] stability	CMC[c] mmoles/liter
$C_{12}H_{25}$	26	<1	63	19.55
$C_{14}H_{29}$	18	40	192	6.65
$C_{16}H_{33}$	35	49	302	2.25
$C_{18}H_{37}$	96	65	542	0.787
Tallow	29	<1	408	---

[a]LSDR = lime soap dispersing requirement.
[b]Calcium ion stability as ppm. $CaCO_3$.
[c]CMC = critical micelle concentration.

TABLE IV

Surface-Active Properties of Sodium Methyl N-alkylsulfosuccinamates

N-alkyl-substituent	LSDR[a]	Krafft point C	Calcium ion[b] stability	CMC[c] mmoles/liter
$C_{12}H_{25}$	7	<1	>1800	4.94
$C_{14}H_{29}$	7	<1	>1800	1.03
$C_{16}H_{33}$	9	25	1270	0.279
$C_{18}H_{37}$	8	36	750	0.082
Tallow-	8	<1	>1800	---

[a]LSDR = lime soap dispersing requirement.
[b]Calcium ion stability as ppm. $CaCO_3$.
[c]CMC = critical micelle concentration.

purged with nitrogen for 10-20 min after which time the system was flushed continuously with nitrogen. Anhydrous sodium sulfite 8.1 g (.064 mole) was added to the flask along with 20.0 g (.064 mole) N-tetradecylmaleamic acid, and the mixture was stirred 2 hr at 80 C. After this period, the clear colorless reaction mixture was treated with 60 ml ethanol and cooled in an ice bath. The precipitated solid was filtered by suction and dried to yield 24.7 g crude product (88% yield). The crude product was extracted in a Soxhlet apparatus overnight with 300 ml ethanol. After drying, the ethanol insoluble disodium N-tetradecylsulfosuccinamate weighed 22.5 g (80% yield). The elemental analyses of the homologous series prepared in this group are shown in Table II.

Surface active properties: Lime soap dispersing requirement was determined by the Borghetty and Bergman (7) procedure. The values indicate the g of reagent required to prevent precipitation of 100 g sodium oleate in 333 ppm hard water. Krafft point is the temperature at which a 1% suspension of compound becomes a clear solution. Calcium ion stability (8) and critical micelle concentration (9) were measured by previously described methods. Surface active properties of the disodium N-alkylsulfosuccinamates are shown in Table III, while those for the corresponding methyl esters are given in Table IV. Detergencies were measured with the aid of a Tergotometer operated at 120 F, 110 cpm for 20 min in 1 liter water of 300 ppm hardness (calculated as $CaCO_3$). Five circular swatches (4 in. diameter) of EMPA 101 cotton, U.S. Testing cotton (UST), and Test Fabric (TF) cotton polyester with a permanent press finish were washed in each beaker. Four washing systems were used: (A) 0.05% test compound, (B) 0.2% test compound, (C) a binary mixture of 0.05% test compound and 0.15% sodium tallowate, (D) a ternary mixture of 0.04% test compound + 0.13% sodium tallowate + 0.03% sodium silicate (SiO_2/Na_2O 1.6:1). Detergency data are summarized in Table V for the sodium methyl N-alkylsulfosuccinamates and the corresponding disodium salts. Detergency values in this table show the results in terms of an increase in reflectance (ΔR) after washing. The control was a phosphate built detergent containing 12.3% phosphorus.

Stability to hydrolysis: The alkaline hydrolysis (10) of sodium methyl N-dodecylsulfosuccinamate was measured by heating 0.005 mole compound in 100 ml 0.05 N NaOH at 100 C. The extent of hydrolysis was measured by the titration of 10 ml aliquots with 0.1N hydrochloric acid (HCL) at fixed time intervals. The ester was almost completely hydrolyzed in 10 min under these conditions. At 60 C, similar results were obtained with ca. 80% of the sample hydrolyzed in 20 min.

RESULTS AND DISCUSSION

Sodium methyl N-alkylsulfosuccinamates (III) were prepared in good yields via the intermediate shown in equation

B. Compounds (II and III) were isolated as crystalline solids and could be purified by crystallization from methanol or aqueous ethanol respectively. Alternate procedures are available for the preparation of N-substituted maleamic acids (equation A) involving the use of toluene (11) or glacial acetic acid (12) as solvents. The method used here was simple; the solvent could be removed easily, and the product air-dried.

Disodium N-alkylsulfosuccinamates (IV) also were obtained in good yield, according to equation D; however, they could not be purified by recrystallization. The crude product obtained by crystallization from aqueous ethanol was found to contain a by-product of low (1-3%) sodium content. The by-product was insoluble in water but was extractable with absolute ethanol. The water-insoluble by-product formed to the extent of 5-12% of the total product when the reactions were run under a nitrogen atmosphere. When the reactions were carried out in air, ca. 2.5 times as much by-product was obtained.

The disodium N-alkylsulfosuccinamates (IV), as shown in Table III, exhibited poor lime soap dispersing requirement with values ranging from 18-96. The Krafft points were generally high (40-65 C) with only the C_{12} and tallow derivatives showing excellent water solubility. Likewise, the calcium ion stabilities of these compounds were poor, the highest value being 540 ppm (as calcium carbonate) for the C_{18} derivative. The critical micelle concentration values of these salts are rather high but do decrease in the expected manner with increasing length of the alkyl chain. In contrast to these results, the introduction of a methyl ester group, as in the sodium methyl N-alkylsulfosuccinamates (III), results in improved surface-active properties, as shown in Table IV. The lime soap dispersing requirement of the esters ranges from 7-9, indicating that they are good lime soap dispersant candidates for soap formulations. Water solubility is increased markedly, the highest Krafft point being 36 C for the C_{18} derivative. Calcium ion stability generally is improved with only the C_{16} and C_{18} esters showing values less than 1800 ppm calcium carbonate. The effect is just as pronounced in the decreased critical micelle concentration values.

Sodium methyl N-alkylsulfosuccinamates were found to be quite unstable to alkaline hydrolysis with sodium hydroxide at both 60 C and 100 C. However the good detergency values obtained with the ternary formulation (Table V) suggest that appreciable hydrolysis did not occur during the wash tests at 120 F.

The surface-active properties of both the esters and the disodium salts were reflected in their detergency behavior. The compounds were screened for detergency to show possible synergism between the components of the ternary detergent formulation. Thus, the detergency data for the test compound by itself at 0.05% and 0.2% concentration gives an indication of effectiveness of the test compound. A comparison between the

TABLE V

Detergency of Sodium Methyl N-alkylsulfosuccinamates

N-alkyl-substituent	Detergency[a] ΔR											
	.05% Compound			.2% Compound			0.2% Binary[b]			.2% Ternary[c]		
	TF	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST
$C_{12}H_{25}$	16	8	6	18	10	7	6	15	6	5	18	4
$C_{14}H_{29}$	22	8	8	26	10	10	20	27	11	19	36	10
$C_{16}H_{33}$	24	4	9	24	7	9	20	22	10	19	35	10
$C_{18}H_{37}$	21	5	9	24	5	12	20	21	9	26	34	12
Tallow	23	5	9	26	9	11	19	23	9	23	34	11
Control[d]	12	8	5	26	40	12	25	39	12	27	38	12

N-alkyl-substituent	Detergency[a] of disodium			N-alkylsulfosuccinamates								
$C_{12}H_{25}$	3	5	6	6	11	8	1	9	2	-1	12	2
$C_{14}H_{29}$	4	4	5	17	34	14	5	16	5	4	23	4
$C_{16}H_{33}$	3	7	5	20	39	14	15	29	8	12	33	7
$C_{18}H_{37}$	4	4	3	19	43	13	13	31	9	17	36	8
Tallow	3	5	4	18	39	13	15	30	9	11	34	8
Control[d]	11	10	6	25	39	12	25	39	12	27	38	12

[a]Detergency values expressed as ΔR (increase in reflectance) were obtained with 1 liter hard water 300 ppm hardness (calculated as $CaCO_3$) containing 1% carboxymethylcellulose based upon total solids. TF = test fabric cotton polyester with a permanent press finish, EMPA = EMPA 101 cotton, and UST = U.S. testing cotton.

[b]0.05% compound + .15% sodium tallowate.

[c]0.04% compound + .13% sodium tallowate + .03% sodium silicate 1.6:1.

[d]The control is a commercial phosphate built detergent tested at the indicated concentrations. It contains 12.3% phosphorus.

with a binary mixture of 25% lime soap dispersant + 75% soap at an 0.2% concentration would indicate synergism between the two components. The ternary mixture represents the combination of 85% the binary formulation with 15% sodium silicate. Development of this tenary formulation has been described in a previous publication (2). Sodium silicate with an SiO_2/Na_2O ratio of 1.6:1 was used, because this ratio gave the most effective silicate builder for soap-based formulations with the lowest alkalinity (2).

The ester derivatives (Table V) with good surface-active properties showed good detergency at 0.05% concentration for TF and UST cloth. At 0.2% concentration or in the binary and ternary formulations, they were comparable to the control in washing TF and UST cloth. However, the synergism between soap and lime soap dispersant observed with previously reported compounds (2) was largely absent and the potentiation of detergency by the silicate builder was slight. Only in the case of the EMPA cloth were we able to observe enhancement of detergency with soap and with silicate. Thus, in spite of the poor EMPA detergency of the esters by themselves, the ternary formulations with all but the C_{12} derivative are about as effective as the control.

On the other hand, the disodium salts (Table V) which possess poorer surface-active properties than the analogous methyl esters show a different detergency pattern. While the detergency of the disodium salts at 0.05% is inferior to that of the esters, the performance at 0.2% on EMPA and UST is superior to that of the ester; and, except for the C_{12} derivative, these values are comparable to that of the control. The disodium salts in combination with soap or in the ternary system show no enhancement of detergency with any of the cloths. They show washing ability in the ternary mixture which is comparable to that of the control only on EMPA cloth. We cannot explain the superior detergency of the disodium salts by themselves at 0.2% over that of the analogous esters.

It is of interest to note that a similar relationship exists between the surface-active properties of disodium α-sulfofatty acids and sodium methyl α-sulfofatty esters (13,14). Whereas disodium α-sulfopalmitate and α-sulfostearate have Krafft points of 76 C and 91 C, respectively, the corresponding methyl esters have values of 29 C and 39 C, respectively. The low water solubility of the disodium salts precluded determination of other surface-active properties. The methyl esters, on the other hand, have lime soap dispersing requirements of 9 with calcium ion stability and critical micelle concentration values comparable to the methyl esters in this study. The stability of sodium methyl α-sulfopalmitate to alkaline hydrolysis (9) is considerably better than that of the methyl esters evaluated here.

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